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Translation of "Variatsionnyy printsip dlya intensivnosti zapreshchennykh perekhodov."
Vestnik Leningradskogo Universiteta, Seriya Fiziki i Khimii,
Vol. 21, No. 16, pp. 26-29, 1966.

NASA TT F-10,619

N 67-25028
(ACCESSION NUMBER) (THRU)
6 1
(PAGES) (CODE)
24
(NASA CR OR TMX OR AD NUMBER) (CATEGORY)
FACILITY FORM 602

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON D.C. FEBRUARY 1967

VARIATIONAL PRINCIPLE FOR THE INTENSITY OF FORBIDDEN TRANSITIONS

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A new variational principle for the calculation of the intensivity of forbidden transitions is given. The stationary value of functional (6) is the matrix element for this transition. The upper and lower boundaries for the matrix elements are given.

1. Introduction

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It is well known that specific difficulties are encountered in theoretical calculations of oscilator strength (Ref. 1). These difficulties are primarily related to the fact that the functions (which are employed to perform the calculations) are as a rule determined from the condition of minimum energy. These functions yield energy values which closely coincide with experiment. However, considerable errors are entailed when they are applied in calculating other quantities -- for example, the probability of a transition. Therefore, it is extremely desirable to have a variational principle which directly yields the value of the transition probability. This variational principle was obtained in a study by Delves (Ref. 2). However, it only pertains to allowed transitions.

The intensity of forbidden transitions was computed in an article by V. M. Buymistrov (Ref. 3). It is our opinion that the variational principle advanced in this article has a significant advantage over the method advanced by V. M. Buymistrov. This advantage will be described in the conclusion.

The oscilator strength P of the spectral line, which corresponds to the transition from the initial state i to the final state f under the influence of the perturbation U, is proportional to the square of the matrix element of the operator U:

$$P = \frac{8\pi^2 m\nu}{h} |(i|U|f)|^2, \tag{1}$$

where ν is the line frequency; m - electron mass.

The quantity U designates the operator of the dipole moment or the moment of any other multipole order. Let H_0 be the Hamiltonian of the system, whose eigen functions will be designated by Ψ_0, and the eigen values will be designated by E_0. We shall assume that $< \Psi_0|U|\Psi'_0 > = 0$ due to the selection rule -- i.e., the transition is forbidden. The perturbation V, which lowers the symmetry of H_0, may lead to a disturbance of the selection rule and to a finite transition probability.

Confining ourselves to the first approximation of the perturbation

* Numbers in the margin indicate pagination in the original foreign text.

theory, we may write

$$\Psi = \Psi_0 + \Psi_1 + \ldots,$$
$$\Psi' = \Psi'_0 + \Psi'_1 + \ldots \tag{2}$$

Corrections of the first approximation may be computed according to the well known formulas of the perturbation theory:

$$\Psi_1 = \sum_n{}' \frac{\Psi_0 | V | \Psi_0^n >}{E_0 - E_0^n} \Psi_0^n, \qquad \text{/27}$$
$$\Psi'_1 = \sum_n{}' \frac{< \Psi'_0 | V | \Psi_0^n >}{E'_0 - E_0^n} \Psi_0^n. \tag{3}$$

Computing the matrix element <i|U|f> by means of (3) and (2), we obtain

$$< i | U | f > = \sum_n{}' \frac{< \Psi_0 | V | \Psi_0^n > < \Psi_0^n | U | \Psi'_0 >}{E_0 - E_0^n} + \tag{4}$$
$$+ \sum_n{}' \frac{< \Psi'_0 | V | \Psi_0^n > < \Psi_0^n | U | \Psi_0 >}{E'_0 - E_0^n}.$$

Equation (4) may be written as follows in a more compact form:

$$< i | U | f > = - \left\{ < \Psi_0 \left| V \frac{1}{H_0 - E_0} U \right| \Psi'_0 > + < \Psi'_0 \left| V \frac{1}{H_0 - E'_0} U \right| \Psi_0 > \right\}. \tag{5}$$

A direct computation according to formula (4) requires a knowledge of the entire spectrum of the operator H_0, which is far from always being the case. Even when this condition is fulfilled, summation of the infinite series (4) is a difficult problem. The variational principle which is advanced does not entail these disadvantages.

2. Variational Principle

Let us examine the functional

$$J(\varphi, \varphi') = \int \varphi (H_0 - E_0) \varphi' d\tau + \int \varphi' V \Psi_0 d\tau + \int \varphi U \Psi'_0 d\tau, \tag{6}$$

where ϕ and ϕ' are trial functions.

It is assumed from this point on that all of the functions and their variations are real. The Euler equations for this functional have the following form

$$\left.\begin{aligned} (H_0 - E_0)\varphi + V\Psi_0 = 0, \\ (H_0 - E_0)\varphi' + U\Psi'_0 = 0. \end{aligned}\right\} \tag{7}$$

Substituting the solution of these equations

$$\left.\begin{aligned} \varphi = -\frac{1}{H_0 - E_0} V\Psi_0, \\ \varphi' = -\frac{1}{H_0 - E_0} U\Psi'_0 \end{aligned}\right\} \tag{8}$$

in the functional (6), we obtain the following expression for the stationary value

$$\text{Stationary value} \quad J(\varphi, \varphi') = -\langle \Psi_0 \left| V \frac{1}{H_0 - E_0} U \right| \Psi_0' \rangle. \tag{9}$$

Thus, the stationary value $J(\phi, \phi')$ gives the first component of the formula (5). In a similar manner, by varying the functional

$$J'(u, u') = \int u (H_0 - E_0') u' d\tau + \int u' U \Psi_0 d\tau + \int u V \Psi_0' d\tau,$$

we obtain the second component of the formula (5).

Let us expand the trial functions ϕ and ϕ' in series of the eigen functions of the operator H_0:

$$\varphi = \sum_n a_n \Psi_0^n, \quad \varphi' = \sum_n b_n \Psi_0^n. \tag{10}$$ /28

We then obtain the following for their variations

$$\delta\varphi = \sum_n \delta a_n \Psi_0^n, \quad \delta\varphi' = \sum_n \delta b_n \Psi_0^n. \tag{11}$$

Let us employ (11) to calculate the second variation of the functional at the point where the first variation equals zero

$$\delta^2 J(\varphi, \varphi') = \sum_n \delta a_n \delta b_n (E_n - E_0). \tag{12}$$

It may thus be seen that no conclusion may be reached regarding the sign of the second variation. Therefore, we may not speak of a maximum or minimum of the functional (6), and we may only speak of its stationary value.

3. Estimates Above and Below

By varying the functional (6), we cannot state that we have approximated the real value from any specific aspect. In other words, if there are several stationary values of $J(\phi, \phi')$ which are computed with different trial functions, it cannot be stated, generally speaking, that any of them is closer to the real value. We may eliminate this disadvantage by formulating the variational problems for computing (5) in the form of maximum and minimum problems.

For this purpose, we may employ the following equation (Ref. 4)

$$\begin{aligned} \langle x | A | y \rangle = &| \langle x_1 | A | x_1 \rangle - \langle x_2 | A | x_2 \rangle | + \\ &+ i | \langle x_3 | A | x_3 \rangle - \langle x_4 | A | x_4 \rangle |, \end{aligned} \tag{13}$$

where

$$\begin{aligned} x_1 &= \frac{1}{2}(x + y), \quad x_3 = \frac{1}{2}(x + iy), \\ x_2 &= \frac{1}{2}(x - y), \quad x_4 = \frac{1}{2}(x - iy). \end{aligned} \tag{14}$$

If we set

$$x = V\Psi_0, \quad y = U\Psi_0', \quad A = \frac{1}{H_0 - E_0},$$

then the matrix element $< \Psi_0 | V \frac{1}{H_0 - E_0} U | \Psi_0' >$ may be expressed in the form of the sum of four matrix elements having the form $< \phi_n | \frac{1}{H_0 - E_0} | \phi_n >$, where ϕ_n are related to $V\Psi_0$ and $U\Psi_0'$ according to formulas (14). As T. K. Rebane (Ref. 5) has shown, we can write the variational principles at the maximum and the minimum in order to calculate matrix elements of the type $< \phi_n | \frac{1}{H_0 - E_0} | \phi_n >$.

Let us introduce the functional

$$K_n(\varphi, \lambda) = \int \left\{ \varphi \left(H_0 - E_0 - \frac{\lambda}{2} \right) \varphi + \right.$$
$$\left. + \frac{2}{\lambda} \left[\left(H_0 - E_0 - \frac{\lambda}{2} \right) \varphi + \varphi_n \right]^2 \right\} d\tau, \tag{15}$$

where λ is a certain numerical parameter. The stationary value of this functional does not depend on λ and equals

Stationary value $K_n(\varphi, \gamma) = \langle \varphi_n | \frac{1}{H_0 - E_0} | \varphi_n \rangle$. (16) /29

The study (Ref. 5) indicated the manner in which the nature of a maximum or a minimum may be attributed to the extremum of the functional (15) by the selection of the parameter λ. We may then write

$$| < \Psi_0 | V \frac{1}{H_0 - E_0} U | \Psi_0' > | \leq \sum_{n=1}^{4} \max K_n(\varphi, \lambda). \tag{17}$$

The inequality (17) provides the upper limit for the desired matrix element. We may readily obtain the lower limit;

$$| < \Psi_0 | V \frac{1}{H_0 - E_0} U | \Psi_0' > | \geq \min K_1(\varphi, \lambda) + \min K_3(\varphi, \lambda) -$$
$$- \max K_2(\varphi, \lambda) - \max K_4(\varphi, \lambda). \tag{18}$$

In a similar way we may write the limits for the second component of formula (5).

4. Conclusions

Thus, the variational principle (6) makes it possible to approximately calculate the probability of forbidden transitions, which are allowed in the first order perturbation theory.

Inequalities (17) and (18) make it possible to obtain the upper and lower limits for the corresponding matrix elements.

If we select functions with parameters as the trial functions, we may relate the calculation of the sum (5) to the solution of algebraic equations, whereas the method advanced in (Ref. 3) requires the solution of a differential

equation. This differential equation is simpler than the corresponding equation of the perturbation theory; however, except for a few special cases, its solution is quite difficult.

In conclusion, the authors would like to express their deep appreciation to P. P. Pavinskiy for supervising the work and T. K. Rebane for valuable discussions.

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Article received April 25, 1966.

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